Mechanism of Reactions of Cobalt(II) Protoporphyrin IX Dimethyl Ester† in Protic and Aprotic, Co-ordinating Solvents‡

Dušanka Pavlović,* Smiljko Ašperger,* and Bujar Domi
Department of Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, Zagreb, Croatia, Yugoslavia

Cobalt(II) protoporphyrin IX dimethyl ester, [$Co^{II}P$], when dissolved (5×10^{-6} mol dm^{-3}) in a co-ordinating, aprotic, highly dielectric solvent(S), in air, rapidly gives [$Co^{II}P(S)$] and [$Co^{II}P(S)(O_2)$] at equilibrium. The Soret absorption maxima of these solutions gradually shift bathochromically, due probably to the formation of [$(S)PCo^{III}(O_2)Co^{III}P(S)$] peroxo-dimers. The Soret shifts (nm) and the reaction rate constant $k_{obs.}$/s^{-1} (25 °C) are as follows: dimethyl sulphoxide (dmso), 403 to 427, 2.6×10^{-6}; dimethyl formamide (dmf), 402 to 424, 1.3×10^{-5}; hexamethylphosphoramide (hmpa), 402 to 426, 3.0×10^{-5}; acetonitrile, 399 to 424, 1.3×10^{-5}; pyridine (py), 402 to 426, 1.5×10^{-4}. On the other hand, the addition of py to a solution of [$Co^{II}P$] in CH_3OH (in air) accelerates the formation of [$Co^{III}P(py)_2$]$^+$ until $k_{obs.}$ (25 °C) reaches 1.5×10^{-3} s^{-1}, which occurs at *ca.* 1 mol dm^{-3} py. The disappearance of [$Co^{II}P$] then slows to a constant rate, which occurs at *ca.* 9 mol dm^{-3} py. Analogous rate maxima appear with all alcohols tested (methanol, ethanol, n-propyl alcohol, ethylene glycol) and with formamide, upon addition of py (or piperidine). However, addition of py to the solutions of [$Co^{II}P$] in dmso or hmpa causes continuous increase of the rate of disappearance of [$Co^{II}P$], indicating that, in these solvents, there is no formation of a bis(ligand) $Co^{III}P$ species.

We have shown previously[1] that the oxidation of cobalt in cobalt(II) protoporphyrin IX dimethyl ester,† [$Co^{II}P$], in the presence of molecular oxygen and amine ligand L [L = pyridine (py), substituted pyridines, piperidine (pip), and imidazole (Him)] proceeds readily in alcoholic media. Even in the absence of amine ligand, [$Co^{II}P$] in methanol undergoes oxidation, yielding [$Co^{III}P(CH_3O)(CH_3OH)$], with a mechanism essentially analogous to that found in the presence of amine ligand;[1] in this case co-ordinated methanol acts as the electron-donor ligand.[2,3]

The solutions of [$Co^{II}P$] in aprotic, non-co-ordinating, solvents (*e.g.* chloroform, dichloromethane, benzene), in the presence of air, are stable and can be used as stock solutions.[1] However, [$Co^{II}P$] dissolved, in the presence of air, in a co-ordinating, aprotic, highly dielectric solvent rapidly gives [$Co^{II}P(S)$] and [$Co^{II}P(S)(O_2)$] (S = solvent) at equilibrium.[4,5] In this paper we study the change of the kinetics and mechanisms of the reactions of [$Co^{II}P$] in mixed protic–aprotic solvents (the aprotic solvent molecule being, at the same time, the electron-donor ligand) in the oxidation of Co^{II} to Co^{III} as well as in the formation of μ-peroxo-species.

Experimental

Materials.—[$Co^{II}P$] was prepared from protoporphyrin IX dimethyl ester (H_2P) (Fluka, purum) and cobalt acetate (Merck, AR grade) according to the literature.[6] The complex was recrystallized from chloroform–methanol and then from benzene; its purity was checked spectroscopically.[4] All solvents were Merck AR grade. Chloroform was washed several times with redistilled water to remove phosgene and other impurities, dried over $CaCl_2$, filtered, and distilled. Pyridine was kept over KOH and freshly distilled before use. Absolute methanol was prepared by the method of Lund and Bjerrum.[7]

Kinetics.—A Cary 16K spectrophotometer with a thermostatted absorption cell (25 ± 0.05 °C) was used for kinetic measurements. The stock solution of [$Co^{II}P$] was 10^{-4} mol dm^{-3} in chloroform. The reaction solutions were prepared by mixing the stock solution with the desired solvent to give 5×10^{-6} mol dm^{-3} of complex and 2—10% (v/v) of chloroform. Variation of chloroform concentration in the indicated range did not affect absorption spectra and kinetics. The kinetics were followed spectrophotometrically by measuring either the rate of decrease of the Soret absorption at *ca.* 400 nm (ε *ca.* 2×10^5 dm^3 mol^{-1} cm^{-1}) or the rate of increase of the absorption peak at *ca.* 427 nm [presumably due to $Co^{III}P(S)$ μ-peroxo-dimers]. The kinetic results were identical at both wavelengths. The kinetics were followed under pseudo-first-order conditions with entering ligands in concentrations several orders larger than the concentration of the complex (5×10^{-6} mol dm^{-3}). All kinetics were followed at least to 99% completion. The rate constants ($k_{obs.}$) are slopes obtained by linear regression of $\ln(A_\infty - A_t)$, or $\ln(A_t - A_\infty)$, on reaction time; A_t and A_∞ are the absorbances at times t and $t = \infty$, respectively. In some cases an Apple II minicomputer was used. Four or five independent kinetic runs were usually performed. Exceptions were long-lasting reactions (followed for up to 20 d) for which only two runs were made. A typical run is shown in Figure 1 which follows the course of the reaction of [$Co^{II}P$] with pyridine in methanol to yield [$Co^{III}P(py)_2$]$^+$; $k_{obs.} = 1.47 \times 10^{-3}$ s^{-1}. The average value obtained from four independent measurements is 1.44×10^{-3} s^{-1}.

Results and Discussion

The oxidation of [$Co^{II}P$] in the presence of molecular oxygen and amine ligands, L, proceeds readily in alcoholic media, according to the equations (1)—(3).[1]

$$[Co^{II}P(ROH)] + L \rightleftharpoons [Co^{II}P(L)] + ROH \qquad (1)$$

---

† (Dimethyl 3,7,12,17-tetramethyl-8,13-divinylporphyrin-2,18-dipropionato)cobalt(II).

‡ Taken from the Thesis submitted by B. Domi in partial fulfilment of the requirements for the M.Sc. degree at the University of Zagreb, 1985. Reported in part at the 23rd International Conference on Co-ordination Chemistry, Boulder, Colorado, U.S.A., August 1984.

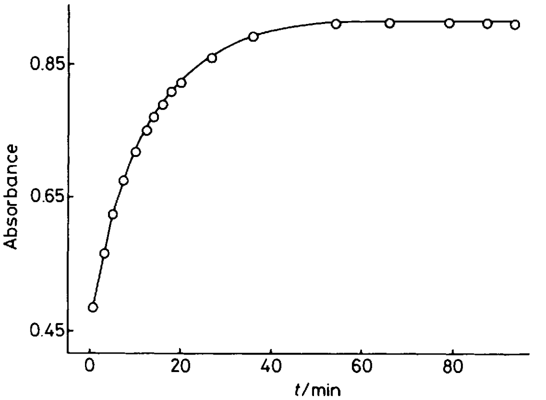

Figure 1. Kinetics of $[Co^{II}P]$ reaction with pyridine in methanol [5% (v/v) of $CHCl_3$, in air]; reaction product, $[Co^{III}P(py)_2]^+$. Starting complex, 5×10^{-6} mol dm^{-3}; py, 0.37 mol dm^{-3}; 25 ± 0.05 °C. The change in absorbance of the reaction product at 420 nm was monitored; $k_{obs.} = 1.47 \times 10^{-3}$ s^{-1} (see Table 2 and Figure 3)

$$[Co^{II}P(L)] + O_2 \rightleftharpoons [Co^{II}P(L)(O_2)] \quad (2)$$

$$[Co^{II}P(L)(O_2)] + HL^+ \longrightarrow [Co^{III}P(L)_2]^+ + HO_2^{\bullet} \quad (3)$$

When L is added (*e.g.* L = pyridine, 10^{-4}—10^{-1} mol dm^{-3}) to a freshly prepared alcoholic [methanol, ethanol, n-propanol, ethylene glycol; all plus 2—5% (v/v) chloroform] solution of $[Co^{II}P]$ (5×10^{-6} mol dm^{-3}, at 25 °C) in the presence of air, the Soret peak of the complex shifts 20 nm bathochromically.[1] This shift was attributed [1] to the spectral changes caused by the rate-determining step (3). In the absence of amine ligand, $[Co^{II}P]$ in methanol also undergoes oxidation, yielding $[Co^{II}P(CH_3OH)]$, in which the co-ordinated methanol acts as the electron-donor ligand. The Soret shift is 14 nm (402 to 416 nm). The formation of $[Co^{II}P(L)(O_2)]$ intermediates, stabilized by the polar and protic properties of the alcoholic media, is widely recognised.[4,5,8–13]

In aprotic, non-co-ordinating solvents, in the presence of L and O_2, $[Co^{III}P(L)_2]^+$ is not formed, a fact that reveals the importance of protons in the elimination of O_2^-. If $[Co^{II}P]$ is dissolved in an aprotic, polar, co-ordinating solvent, in the presence of air but in absence of an amine ligand, the reaction proceeds 2—3 orders of magnitude slower than the formation of $[Co^{III}P(L)_2]^+$. The aprotic co-ordinating solvents we used were dimethyl sulphoxide (dmso), acetonitrile (an), dimethylformamide (dmf), and hexamethylphosphoramide (hmpa). Figure 2 shows the spectral changes that occur during the reaction of $[Co^{II}P]$ and dmso. The Soret shifts caused by reaction of $[Co^{II}P]$ in the above aprotic solvents and the reaction rates are given in Table 1. We ascribe the Soret shifts to the formation of $[(S)PCo(O_2)CoP(S)]$, by analogy with the reaction of amine complexes of $[Co^{II}P]$ with oxygen in toluene believed[4] to be peroxo-bridged complexes. The average Soret shift in Table 1 is *ca.* 24 nm, as compared with a shift of 20 nm in the formation of $[Co^{III}P(L)_2]^+$. Moreover, the rate of formation of bis(ligand)-cobalt(III) complexes is larger in solvents with higher dielectric constants (the charge separation is essential for superoxide elimination), while the data in Table 1 reveal just the opposite effect of the solvent polarity.

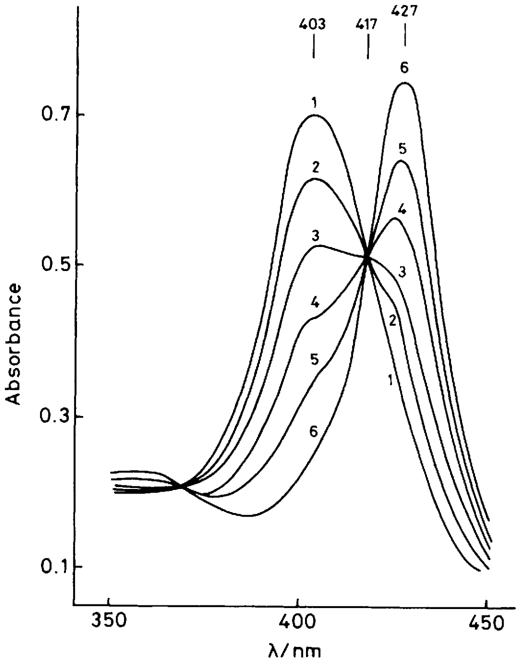

Figure 2. Spectral changes during the reaction of a solution (5×10^{-6} mol dm^{-3}) of $[Co^{II}P]$ in dmso [3% (v/v) of chloroform, in air] with dmso and molecular oxygen at 25 ± 0.02 °C. Scans (1—6) are numbered consecutively after 0, 3, 5, 7, 9, and 15 d

Table 1. Rates of Soret shifts of $[Co^{II}P]$ in various aprotic, co-ordinating solvents at 25 ± 0.05 °C

Solvent	Soret shift (nm)	$10^5 k_{obs.}$*/s^{-1}	Solvent dielectric constant (25 °C)
dmso	403 to 427	0.25 (0.02)	48.9
an	399 to 424	1.30 (0.08)	37.5
dmf	402 to 424	1.32 (0.09)	36.7
hmpa	402 to 426	3.0 (0.15)	29.6

* Uncertainties are standard errors of the mean.

These results suggest that there was no O_2 elimination. The dimer can be formally written as $[(S)PCo(O_2)CoP(S)]$, where the cobalt is presumably Co^{III} and O_2 is present as peroxide. Whatever the structure, the electron density on dioxygen appears to be greatly delocalised, as inferred from the solvent effect presented in Table 1. Likewise, the brown, diamagnetic complex $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$, where the O–O bridge bond length is 1.47 Å (as in peroxide[14]) may be thought of as having a $Co^{3+}(O_2^-)Co^{3+}$ unit.[15] The unit $Co^{\delta+}(O_2)Co^{\delta+}$ involving superoxide {as in green, paramagnetic[16] ($S = \frac{1}{2}$) $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$} is less likely in the present complex, as this unit would give the complex a positive charge. Thus, the complex would form more easily in solvents of higher polarity. We found this not to be the case.

It is also of note that the α-peak of methanolic solutions of $[Co^{III}P(L)_2]^+$ in the absorption spectra is always somewhat more intense than the β-peak. The opposite is true with alcoholic solutions of the supposed μ-peroxo-dimer.

Dependence of the Rate of Reactions of $[Co^{II}P]$ *with Pyridine on Pyridine Concentration in Protic Solvents.*—The rates in alcoholic solutions reach maximum values at 0.5—1.0 mol dm^{-3} of py (Figure 3). Analogous rate maxima were obtained in formamide solutions. The ascending parts of the curves in Figure 2 correspond to the overall reaction, (4), while the

$$[Co^{II}P(S)] + py \xrightarrow[O_2]{solvent} [Co^{III}P(py)_2]^+ + HO_2^{\bullet} \quad (4)$$

descending part, we believe, reflects the formation of the

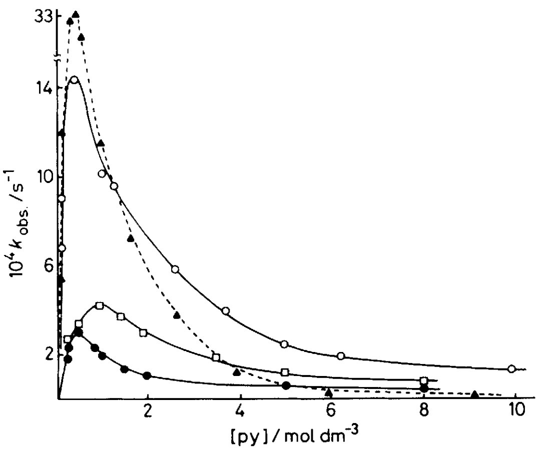

Figure 3. Dependence of the rate of reaction of [$Co^{II}P$] (5 × 10^{-6} mol dm^{-3}) and pyridine on concentration of py in ethylene glycol (▲), methanol (○), ethanol (□), and n-propyl alcohol (●); temperature, 25 ± 0.02 °C

Table 2. Maximum rates of reaction of [$Co^{II}P$] (5 × 10^{-6} mol dm^{-3}) with pyridine (0.5—1.0 mol dm^{-3}) in protic solvents, at 25 ± 0.05 °C

Solvent	Dielectric constant (25 °C)	$10^4 k_{obs.}$*/s^{-1}
Formamide	109	280 (14)
Ethylene glycol	37.7	33 (1.5)
Methanol	32.6	14.4 (0.7)
Ethanol	24.3	4.2 (0.2)
n-Propyl alcohol	20.1	3.0 (0.2)

* Uncertainties are standard errors of the mean.

binuclear complex, [$(py)PCo^{III}(O_2)Co^{III}P(py)$]. The formation of the $Co^{III}(py)_2$ complex is favoured in protic solvents, and the formation of the μ-peroxo-dimer is favoured in aprotic solvents. In Table 2 are presented the maximum rates in protic solvents, showing that the higher the dielectric constant the higher the maximum rate.

The measurements of the dependence of the rate of reaction of [$Co^{II}P$] with piperidine on piperidine concentration in methanol show that the maximum rate is at 1 mol dm^{-3} pip, when $k_{obs.}$ = 0.01 s^{-1}; the rate is *ca.* 7.5 times larger than that with pyridine in methanol (see Table 2). This is to be expected because pip is a more basic entering ligand (pK_a: py, 5.2; pip, 11.1 [17]) and the increased entering reagent basicity increases the rate of formation of [$Co^{III}P(L)_2$]$^+$.[1,18]

In aprotic solvents (dmso, hmpa, dmf, an), the reaction of [$Co^{II}P$] with py does not show a rate maximum. For dmso this can be seen from Figure 4. In this solvent, [$Co^{III}P(py)_2$]$^+$ apparently does not form, as there are no protons to enable elimination of O_2^-. Here, the only reaction product, a bridged dimer, is most probably [$(py)PCo^{III}(O_2)Co^{III}P(py)$]. The overall rates (Figure 4) are *ca.* 10^2—10^3 times lower than in protic solvents. Very similar results were obtained when [$Co^{II}P$] and py reacted in hmpa and dmf.

Conclusions

As shown previously,[4] [$Co^{II}P$] dissolved in an aprotic, apolar, non-co-ordinating solvent (benzene, toluene, dichloromethane; 5 × 10^{-3} mol dm^{-3}) does not react with atmospheric oxygen. If amine ligands are added, the reaction with molecular oxygen takes place and μ-peroxo-complexes are formed.[4] We have shown that [$Co^{II}P$], when dissolved in aprotic, polar, co-ordinating solvents, yields μ-peroxo-dimers, even in the absence of any amine ligand. The co-ordinated solvent molecule acts in the same way as the amine ligands by virtue of their electron-donating abilities. In a typical protic solvent such as methanol, when it contains the methoxide ion in high concentration (*ca.* 0.5 mol dm^{-3}), [$Co^{II}P$] gives μ-methoxo-dimers.[19] It can be concluded that the formation of [$Co^{III}P(L)_2$]$^+$ complexes requires not only oxygen but also protons for subsequent O_2^- elimination.[1,20] In the absence of oxygen (argon atmosphere) [$Co^{II}P$], when dissolved in methanol, is stable, even in presence of amine ligands. It appears logical, therefore, that [$Co^{II}P$], when dissolved in an aprotic, co-ordinating solvent, yields μ-peroxo-dimers and not cobalt(III) disolvento-complexes, due to lack of protons.

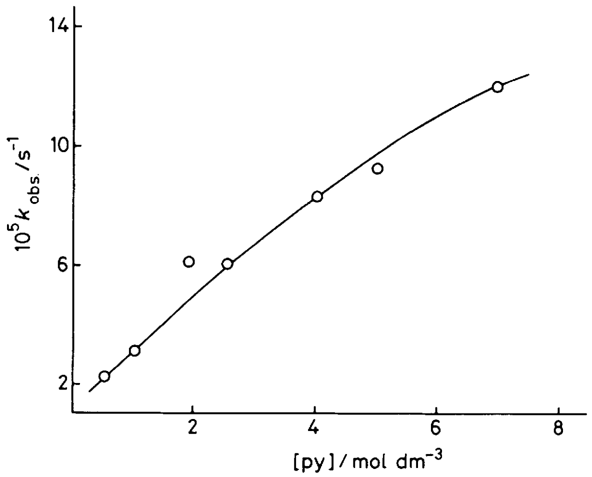

Figure 4. Dependence of the rate of reaction of [$Co^{II}P$] and py in dmso on concentration of py; conditions as in Figure 1

References

1 Z. Dokuzović, Xh. Ahmeti, D. Pavlović, I. Murati, and S. Ašperger, *Inorg. Chem.*, 1982, **21**, 1576.

2 Z. Dokuzović, D. Pavlović, S. Ašperger, and I. Murati, *J. Chem. Soc., Chem. Commun.*, 1984, 1060.

3 D. Pavlović, S. Ašperger, Z. Dokuzović, B. Jurišić, Xh. Ahmeti, M. Sertić, and I. Murati, *J. Chem. Soc., Dalton Trans.*, 1985, 1095.

4 D. V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Am. Chem. Soc.*, 1973, **95**, 1142; 1974, **96**, 1358; D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *ibid.*, 1973, **95**, 1796.

5 F. Basolo, B. M. Hoffman, and J. A. Ibers, *Acc. Chem. Res.*, 1975, **8**, 384, and refs. therein.

6 J. E. Falk, 'Porphyrins and Metalloporphyrins,' Elsevier, Amsterdam, 1964, vol. 2, p. 139.

7 H. Lund and J. Bjerrum, *Ber. Dtsch. Chem. Ges.*, 1931, **64**, 210.

8 F. A. Walker, D. Beroiz, and K. M. Kadish, *J. Am. Chem. Soc.*, 1976, **98**, 1484; F. A. Walker, *ibid.*, 1970, **92**, 4234.

9 J. A. Cohen and W. S. Caughey, *Biochemistry*, 1968, **7**, 636.

10 B. S. Tovrog, D. J. Kitko, and R. S. Drago, *J. Am. Chem. Soc.*, 1976, **98**, 5144.

11 R. S. Drago, T. Bengelsdijk, J. A. Breese, and J. P. Cannady, *J. Am. Chem. Soc.*, 1978, **100**, 5374.

12 R. Dreos, G. Tauzher, G. Costa, and M. Green, *J. Chem. Soc., Dalton Trans.*, 1975, 2329.

13 P. Zanello, R. Cini, A. Cinquantini, and P. L. Orioli, *J. Chem. Soc., Dalton Trans.*, 1983, 2159.

14 A. G. Sykes and J. A. Weil, *Prog. Inorg. Chem.*, 1970, **13**, 1.

15 W. P. Schaefer, *Inorg. Chem.*, 1968, **7**, 725.

16 K. F. Purcell and J. C. Kotz, 'Inorganic Chemistry,' W. B. Saunders, Philadelphia, 1977, pp. 746—747.
17 R. C. Weast (ed.), 'Handbook of Chemistry and Physics,' 53rd edn., The Chemical Rubber Co., Cleveland, Ohio, 1972—1973, p. D-117.
18 D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Am. Chem. Soc.*, 1973, **95**, 1796.
19 D. Pavlović, S. Ašperger, and Xh. Ahmeti, unpublished work.
20 R. J. McConnel, B. G. Overell, V. Petrov, and B. Sturgeon, *J. Pharm. Pharmacol.*, 1953, **5**, 179.

Received 29th October 1985; *Paper* 5/1904